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Developing Terminal Phosphinidene Complexes

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Abstract:

In **Chapter 1** the syntheses, properties, and reactivities of nucleophilic phosphinidene complexes $L_nM=P-R$ are reviewed. Emphasis is placed on the electronic tuning of this emerging class of phosphorus reagents, using different ancillary ligands and coordinatively unsaturated transition metal moieties. The difference in applicability of the established stable 18-electron and transient 16-electron phosphinidenes is addressed.

In **Chapter 2** the synthesis and reactivity of NHC-functionalized Ru phosphinidene $(\eta^6-Bz)(IIPr_2Me_2)Ru=PMes^*$ is described. The influence of the stabilizing ligand (PPh_3 vs NHC) and the relative σ -donor/ π -acceptor ability of these ligands bonded to the nucleophilic phosphinidene complexes are investigated computationally.

The scope of the dehydrohalogenation–ligation sequence using NHCs both as Brønsted base and as stabilizing ligand has been successfully extended in **Chapter 3** by the synthesis of novel ruthenium, osmium, and rhodium phosphinidene complexes. An extensive computational analysis of the Group 7-9 transition metal complexed phosphinidenes revealed Re, Rh, and Ru as the most reactive transition metals of the Group 7-9 triads.

In **Chapter 4** *in-situ*-generated 16-electron complex $[(Cp^*)Ir=P-R]$ ($R = Mes, Mes^*, Dmp$) were reacted with isocyanide $ArN\equiv C$ yielding isolable phosphinidene complexes $(Cp^*)(ArN\equiv C)Ir=P-R$, which are prone to [1+2] cycloaddition with a second isocyanide $Ar'N\equiv C$ to afford novel iridaphosphirane complexes $[Cp^*(Ar-N\equiv C) \overline{IrPARC} = NAr']$. For the imido analogue $[(Cp^*)Ir\equiv N-tBu]$ of Bergman a different mechanism is found with isocyanides.

In **Chapter 5** the synthesis, mechanism, and reactivity of the novel η^3 -diphosphavinylcarbene complex, a diphosphorus analogue of the versatile Dötz intermediate, is presented. The product obtained with the less congested $tBuC\equiv P$ was shown to convert via an unprecedented rearrangement to the novel 1,3-diphospha-3*H*-indene complex.